AD-A173 641 ORGANOPHOSPHAZENES 21 THE SYNTHESIS OF (ALPHA-METHYLETHENYL)-PHENYLFLUOROCYCLOTRIPHOSPHAZENES (U) VERMONT UNIV BURLINGTON DEPT OF CHEMISTRY 1/1

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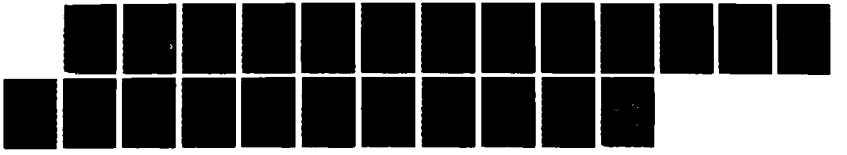

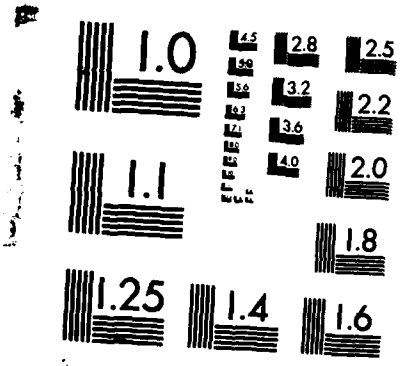

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OFFICE OF NAVAL RESEARCH

Contract N00014-85-K-0558

Task No. NR413C012-01

TECHNICAL REPORT NO. 4

Organophosphazenes. 21. The Synthesis of (α-Methylethenyl)-phenylfluorocyclotriphosphazenes

by

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Accepted for Publication

in

Inorganic Chemistry

University of Vermont
Department of Chemistry
Burlington, VT 05405

October 3, 1986

SECURITY CLASSIFICATION OF THIS PAGE AD-A173 641

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION: Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT: Available for public release Distribution unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S): Technical Report No. 4	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION: University of Vermont; 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION: ONR
6c. ADDRESS (City, State, and ZIP Code): Department of Chemistry, Cook Physical Science Building, Burlington, VT 05405	7b. ADDRESS (City, State, and ZIP Code): Office of Naval Research, Arlington, VA 22217
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: ONR; 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code): Office of Naval Research, 800 N. Quincy, Arlington, VA 22217	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. N00014-85; PROJECT NO. K-0558; TASK NO. NR 413C012; WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)
Organophosphazenes. 21. The Synthesis of (α-Methethenyl)phenyl-fluorocyclotriphosphazenes

12. PERSONAL AUTHOR(S)
Jonathan C. Shaw and Christopher W. Allen

13a. TYPE OF REPORT: Preprint	13b. TIME COVERED: FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day): 1986/10/3	15. PAGE COUNT: 17

16. SUPPLEMENTARY NOTATION
Submitted for publication in Inorganic Chemistry

COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
GROUP	SUB-GROUP	cyclophosphazenes; ^{13}C and ^{31}P nmr; arylphosphazenes; α-methylstyrenes

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The reactions of m and p - (α - Methylethenyl) phenyllithium with hexafluorocyclotriphosphazene, $N_3P_3F_6$, lead to the formation of the series of (α-methylethenyl) phenylfluorocyclotriphosphazenes, $N_3P_3F_{6-n}[C_6H_4C(CH_3)=CH_2]_n$ (n=1,2). At the bis stage of substitution both the geminal and non-geminal derivatives are obtained with the cis non-geminal species predominating. The cis to trans ratio is dependent on the position (meta or para) of the α-methylethenyl substituent on the phenyl ring. A model for the observed stereochemistry of the reaction is presented. The new compounds were characterized by mass spectrometry along with NMR (^1H, ^{13}C, ^{19}F, ^{31}P) and IR spectroscopy. Examination of the ^{13}C NMR spectra shows the modification in the phenyl charge distribution induced by the fluorophosphazene moiety.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT: ☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION: Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code); 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted. All other editions are obsolete. SECURITY CLASSIFICATION OF THIS PAGE

Contribution from the Department of Chemist
University of Vermont
Burlington, Vermont 05405

Organophosphazenes. 21. The Synthesis of (α-Methylethenyl)phenylfluorocyclotriphosphazenes.[1]

Jonathan C. Shaw and Christopher W. Allen*

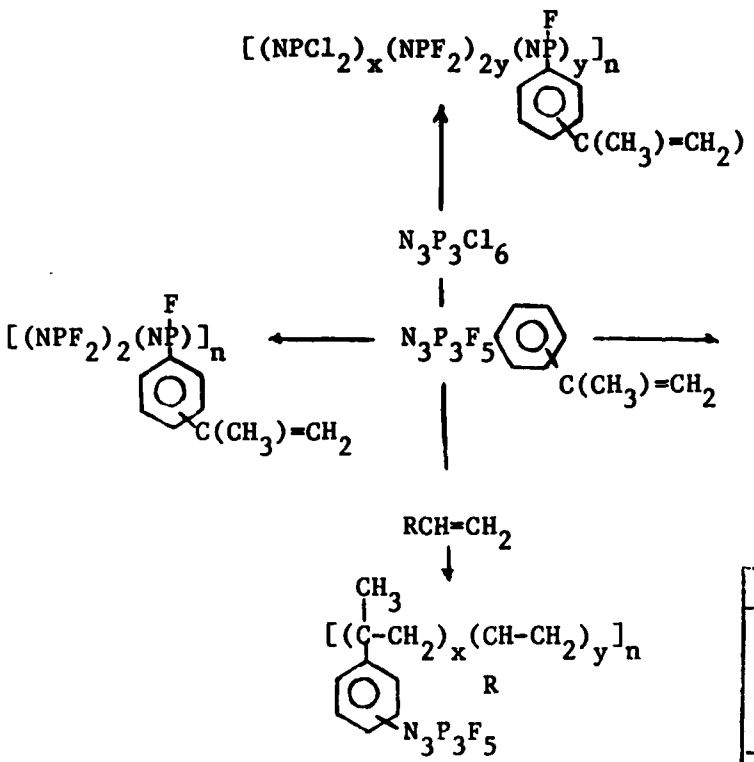
Received:

The reactions of m and p - (α - Methylethenyl) phenyllithium with hexafluorocyclotriphosphazene, $N_3P_3F_6$, lead to the formation of the series of (α - methylethenyl) phenylfluorocyclotriphosphazenes, $N_3P_3F_{6-n}[C_6H_4C(CH_3)=CH_2]_n$ (n= 1,2). At the bis stage of substitution both the geminal and non-geminal derivatives are obtained with the cis non-geminal species predominating. The cis to trans ratio is dependent on the position (m vs p) of the α-methylethenyl substitutent on the phenyl ring. A model for the observed stereochemistry of the reaction is presented. The new compounds were characterized by mass spectrometry along with NMR (^1H, ^{13}C, ^{19}F, ^{31}P) and IR spectroscopy. Examination of the ^{13}C NMR spectra shows the modification in the phenyl charge distribution induced by the fluorophosphazene moiety.

Introduction

Organophosphazenes have become popular targets for synthesis in recent years [2-5] because of the inherent interest in this class of compounds and for more practical reasons, such as the development of new phosphazene monomers which may be transformed into novel polymers.[3,4] Fundamental aspects of interest involve questions involving the factors which control the stereochemistry of the substitution reactions leading to organophosphazenes [2,6,7] and the synthesis of unique materials such as organometallic phosphazene derivatives.[4,5] Novel polymers from these monomers include polyphosphazenes with organic or organometallic substituents [4,8] and organic copolymers with cyclophosphazenes

as substituents.[3] Monomers for this latter type of polymer have been olefinic phosphazenes. The high polarity of the olefin induced by the cyclophosphazene[9-11] has caused some difficulties in the polymerization process.[12] One approach to the successful reduction of olefinic polarity in these systems, which we have reported, is the introduction of an electron donating function on the olefin to counter balance the electron withdrawing effect of the phosphazene.[7,13] An alternative approach to the problem of phosphazene induced polarity is the introduction of an insulating function between the phosphazenes and the olefin. In this paper, we present the synthesis of α-methylethenyl phosphazenes with a phenyl group between the phosphorus and olefinic centers i.e. phosphazene derivatives of α-methylstyrene. These materials can potentially polymerized or copolymerized by two different routes as shown in scheme 1. The phosphazene ring



Scheme 1

processes would lead to linear phosphazene polymers while addition polymerzation of the olefinic center would lead to carbon chain polymers with the cyclophosphazene as a substituent. The addition copolymerization of (α-methylethenyl) pentafluorocyclotriphosphazenes with certain organic olefinic comonomers has been studied and will be reported in a subsequent publication.

Experimental

Materials and Methods. Hexafluorocyclotriphosphazene, $N_3P_3F_6$ (1)[14], obtained from hexachlorocyclotriphosphazene (Firestone Corp.), and both m and p - bromo-α-methyl styrene[15], (α-methylethenyl)phenyl bromide, were produced according to previously published procedures. n-Butyl lithium (1.55m in hexames, Aldrich) was used as received. Diethyl ether was distilled from sodium/benzophenone, while petroleum ether (bp 30-60°C) was distilled from sodium ribbon and stored over molecular sieves. NMR spectra (in $CDCl_3$) were recorded on a Brüker WM 250 spectrometer operating at 250.1 (^1H), 62.9 (^{13}C), 235.2 (^{19}F), and 101.2 (^{31}P) Mllz. Tetramethyl silane (^1H and ^{13}C) and hexafluorobenzene (^{19}F) were used as internal standards, whil. 85% H_3PO_4 (^{31}P) was employed as an external reference. Infrared spectra were obtained as thin films (NaCl disks) on a Nicolet 6000 series spectrophotometer. Mass spectra and G.C. mass spectra were recorded on a Finnigan 4610 spectrometer operating at 70 eV and equipped with a 30m capillary column coated with SE-30. Other G.C. experiments were conducted on a Hewlett-Packard 5700A instrument equipped with a Chromasorb W (SE-30) column. Elemental analysis were conducted by Robertson Laboratory, Inc.

All reactions were performed in an anhydrous environment under a stream of N_2 and were magnetically stirred. Syringe techniques were used to transfer reagents where applicable.

Preparation of $N_3P_3F_5$ (C_6H_4-p-$C(CH_3)=CH_2$) (2). A previously described air sensitive reagent reaction vessel [16] was charged with 50 ml of diethyl ether and 37.3 ml (1.55 M 0.0578 mol) of n-butyl lithium in hexanes, and cooled to 0°C. A solution of 10.05 g (0.051 mol) of p-bromo-α-methyl styrene in 150 ml of diethylether was than added slowly to the butyl lithium solution. The mixture was allowed to stir an additional 2 hours after all the reagent had been added. The lithiated α-methyl styrene was then transfered dropwise to a solution of 12.70 g (0.051 mol) of $N_3P_3F_6$,1, in 200 ml diethyl ether at 0°C. The reaction was allowed to warm to room temperature and stirred overnight. After removal of the solvent, petroleum ether was added to precipitate the lithium salts, which were subsequently removed by filtration through diatomaceous earth. The petroleum ether was then removed to give a yellowish oil, which, upon distillation, gave 9.72 g (54.9% of theory) of a clear liquid (bp 50-52°C @ 0.02 mm Hg). Anal. Calcd. for $C_9H_9N_3P_3F_5$: C, 31.14; H, 2.61; mol. wt. 347. Found: C, 30.85; H, 2.75; mol. wt. 347 (mass spectrum). [17]

^1H NMR:[18] δ_{CH_3} 2.16 (s,3H); δ_{Ha} 5.22 (s,1H); δ_{H_6} 5.45 (s,1H); δ_{Hom} 7.83 (d of d,2H), J_{HH}= 8.3, $^3J_{PH}$ = 15.9; δ_{Hm} 7.58 (d of d,2H), $^1J_{HH}$ = 8.3, $^4J_{PH}$ = 4.7. ^{13}C NMR:[19] δ_{C_1} 125.20; J_{PC} = 210; δ_{C_2} = 130.96, $^2J_{PC}$ = 12.9; δ_{C_3} 126.21, $^3J_{PC}$ = 18.3; δ_{C_4} 147.56. $^4J_{PC}$ = 3.3; δ_{C_5} 142.38; δ_{C_6} 115.86; δ_{C_7} 21.50. ^{19}F NMR: δ_{PFR} - 54.99, $^1J_{FP}$ = 986; δ_{PF_2}-cis -69.96, $^1J_{FP}$ = 916; δ_{PF_2}-trans -71.97, $^1J_{FP}$ = 911. ^{31}P NMR: δ_{PFR} 35.44, $^1J_{PF}$ = 985, $^2J_{PP}$ = 78.1, $^3J_{PF}$ = 19.5; δ_{PF_2} 9.25. $^1J_{PF}$ = 913, $^2J_{PP}$ 78.1. IR:[20] 1630 (m, νc=c), 1603 (m, νc,=c), 1268 (vs $\nu_{P=N}$), 945 (s, $\nu_{PF,asym}$), 835 (s, $\nu_{PF,sym}$)

Preparation of $N_3P_3F_5(C_6H_4$-m-$C(CH_2)=CH_2)$ (3). The preparation was allowed to proceed as above with the exception that m-bromo-α-methyl styrene is used in place of p-bromo-α-methyl styrene. In a typical experiment the following quantities of materials were used: m-bromo-α-methyl styrene, 12.84 g (0.0652 mol) in 200 ml diethylether; n butyl lithium, 48.1 ml (1.55 m in hexemes, 0.0720 mol); and 1, 16.30 g (0.0655 mol) in 200 ml diethyl ether. The resulting oil was distilled to give 11.23 g (49.6% of theory) of a clear liquid (bp. 75-77°C @ 0.04 mm Hg). Calcd. for $C_9H_9N_3P_3F_5$: C, 31.14; H, 2.61; mol wt. 347. Found: C, 31.47; H, 2.70; mol wt. 347 (mass spectrum).[17]

^1H NMR[18] : δ_{CH_3} 2.18 (s,3H); δ_{Ha} 5.21 (s,1H); δ_{H_6} 5.44 (s,1H); δ_{Ho} 7.80 (m,1H), $^3J_{PH}$ = 17.4; $\delta_{Ho'}$ 7.95 (m,1H); $^3J_{PH}$ 15.9; δ_{Hm} 7.51 (m,1H); δ_{Hp} 7.77 (m,1H). ^{13}C NMR[21] : δ_{C_1} 126.86, $^1J_{PC}$ = 205; δ_{C_2} 127.64, $^2J_{PC}$ = 13.0; $\delta_{C_{2'}}$ 129.43, $^2J_{PC}$ = 12.6; δ_{C_3} 142.60, $^3J_{PC}$ = 16.7; $\delta_{C_{3'}}$ 129.13, $^3J_{PC}$ 18.2; δ_{C_4} 131.44, $^4J_{PC}$ = 3.1; δ_{C_5} 142.10; δ_{C_6} 114.80; δ_{C_7} 21.64. ^{19}F NMR: δ_{PFR} -55.12, $^1J_{FP}$ = 941; δ_{PF_2}-cis -69.93, $^1J_{FP}$ = 905; δ_{PF_2}-trans-71.99, $^1J_{FP}$ = 905. ^{31}P NMR: δ_{PF_2} 9.31, $^1J_{PF}$ = 909, $^2J_{PP}$ 76.9; δ_{PFR} 35.58, $^1J_{PF}$ = 989, $^2J_{PP}$ 76.9, $^3J_{PF}$ 19.5. IR:[20] 1632 (m, νc=c), 1607 (m, νc=c), 1270 (vs, $\nu_{P=N}$), 943 (s, $\nu_{PF,asym}$), 837 (s, $\nu_{PF,sym}$).

Preparation of $N_3P_3F_4(C_6H_4$-p-$C(CH_3)=CH_2)_2$ (4). The preparation was allowed to proceed as above, except that two equivalents of n-butyl lithium and p-bromo-α-methyl styrene are employed. In a typical experiment, the following quantities were used: p-bromo-α-methyl styrent, 9.85 g (0.0500 mol) in 200 ml Et_2O; n-butyl lithium, 35.5 ml (1.55 m in hexames, 0.0550 mol), and 1, 6.23 g (0.0250 mol) in 200 ml of diethyl ether. After removal of the lithium salts, the oil was subjected to flash chromatography[22] (petroleum ether) to give 9.50 g (42.7% of theory) of a mixture of isomers. Anal. Calcd. for $C_{18}H_{13}N_3P_3F_4$: C, 48.55; H, 4.07; mol wt. 445. Found: C, 47.69; H, 4.13; mol. wt. 445 (mass spectrum).[17] A gas chromatographic analysis of the mixture revealed the isomer ratio to be

1:6.1:1.5 for the geminal, cis, and trans isomers, respectively. Unfortunately, while the cis isomer could be recrystallized from a dilute heptane solution, the geminal and trans isomers resisted further separation. The melting point of the cis isomer was 104.0–105.1 °C Anal. Calcd. for $C_{18}H_{18}N_3P_3F_4$: C, 48.55; H, 4.07; mol. wt. 445. Found: C, 48.13; H, 4.20; mol. wt. 445 (mass spectrum)[17] ^1H NMR (mixture of isomers):[18] δ_{CH_3} 2.13–2.16; δ_{Ha} 5.17–5.22; δ_{Hb} 5.42–5.47; δ_{Har} 7.51–7.95. Cis -4 ^1H NMR:[18] δ_{CH_3} 2.16 (s,3H); δ_{Ha} 5.22 (s,1H); δ_{Hb} 5.46 (s,1H); δ_{Ho} 7.85 (d of d, 2H), J_{HH} = 8.3, $^3J_{PH}$ = 15.5; δ_{Hm} 7.58 (d of d, 2H), $^1J_{HH}$ = 8.3, $^3J_{PH}$ = 4.2. ^{19}F NMR: δ_{PFR} -52.39, $^1J_{FP}$ 984; δ_{PF_2}-cis -68.17, $^1J_{FP}$ = 920, $^2J_{FF}$ = 77.5; δ_{PF_2}-trans -71.71; $^1J_{FP}$ = 899, $^2J_{FF}$ = 77.5, $^3J_{FP}$ = 18.8, $^4J_{FF}$ = 12.1. ^{31}P NMR: δ_{PF_2} 7.25, $^1J_{PF}$ = 919, $^2J_{PP}$ 61.1, $^3J_{PF}$ = 2.9; δ_{PFR} 33.50; $^1J_{PF}$ =974, $^2J_{PP}$=61.1, $^3J_{PF}$ = 3.1

Trans-4 ^{19}F NMR: δ_{PFR} -51.93, $^1J_{FP}$ 986; δ_{PF_2} -70.43, $^1J_{FP}$ = 932. ^{31}P NMR: δ_{PF_2} 6.03, $^1J_{PF}$ = 912, $^2J_{PP}$ = 68.8, $^3J_{PF}$ = 7.2; δ_{PFR} 33.67, $^1J_{PF}$ = 973, $^2J_{PP}$ = 68.8, $^3J_{PF}$ = 9.6

Gem-4 ^{19}F NMR: δ_{PF_2} -70.44, $^1J_{FP}$ = 891. ^{31}P NMR: δ_{PF_2} 8.30, $^1J_{PF}$ = 878, $^2J_{PP}$ = 52.0; δ_{PR_2} 26.35, $^2J_{PP}$ = 52.0, $^3J_{PF}$ = 6.3.

Preparation of $N_3P_3F_4(C_6H_4$-m-$C(CH_3)=CH_2)_2$(5). This preparation was allowed to proceed as above with the exception that m-bromo-α-methyl styrene is used in place of the p-bromo analog. In a typical experiment, the following quantities of reagents were used: m-bromo-α-methyl styrene, 7.88 g (0.040 mol) in 200 ml diethyl ether; n-butyl lithium, 36.0 ml (1.23 m in hexames, 0.0443 mol); and 1, 5.00 g (0.0200 mol) in 200 ml diethyl ether. The salt-free oil was purified via flash chromatography (petroleum ether) to give 4.59 g (51.5% of theory) of a mixture of isomers. Aval. Calcd. for $C_{18}H_{18}N_3P_3F_4$: C, 48.55; H, 4.07; mol. wt. 445. Found: C, 47.24; H, 4.07; mol wt. 445 (mass spectrum).[17] Further preparative

level separation of the isomers could not be achieved. A gas chromatographic analysis of the mixture revealed the ratio of geminal to cis to trans ratio of 1:1.8:1.1. ^{1}H NMR [18] (mixture of isomers): δ_{CH_3} 2.14-2.19; δ_{Ha} 5.16-5.20, δ_{H_6} 5.43-5.48; δ_{Ha} 7.41-8.02.

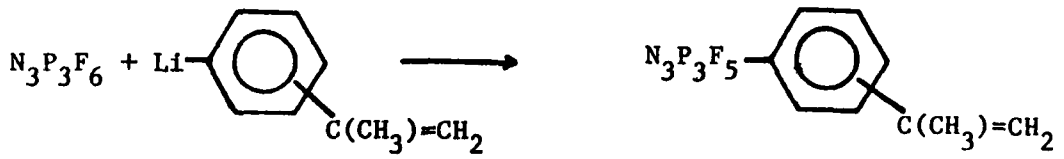
Cis-5 ^{19}F NMR: δ_{PFR} -52.73, $^{1}J_{FP}$ = 995; δ_{PF_2}-cis -68.50, $^{1}J_{FP}$ = 909; δ_{PF_2}-trans -72.01, $^{1}J_{FP}$ = 903. ^{31}P NMR δ_{PF_2} 7.29, $^{1}J_{PF}$ = 924, $^{2}J_{PP}$ = 62.6, $^{3}J_{PF}$ = 3.1; δ_{PFR} = 33.64, $^{1}J_{PF}$ = 994, $^{2}J_{PP}$ = 62.6, $^{3}J_{PF}$ = 8.7

trans-5 ^{19}F NMR: δ_{PFR} -51.88, $^{1}J_{FP}$ = 989; δ_{PF_2} -70.67, $^{1}J_{FP}$ = 926. ^{31}P NMR: δ_{PF_2} 5.42, $^{1}J_{PF}$ = 911, $^{2}J_{PP}$ 67.6, $^{3}J_{PF}$ 7.9; δ_{PFR} 33.64, $^{1}J_{PF}$ = 994, $^{2}J_{PP}$ = 67.6, $^{3}J_{PF}$ = 14.5

geminal-5 ^{19}F NMR: δ_{PF_2} -70.51, $^{1}J_{PF}$ = 900. ^{31}P NMR: δ_{PF_2} 8.48, $^{1}J_{PF}$ = 914, $^{2}J_{PP}$ = 58.4; δ_{PR_2} 26.69, $^{2}J_{PP}$ 58.4, $^{3}J_{PF}$ 11.68 IR [20] (mixture of isomers): 1631 (m, $\nu_{C=C}$), 1602 (m, $\nu_{C=C}$), 1246 (vs, $\nu_{P=N}$), 925 (s, $\nu_{PF,sym}$).

Results and Discussion

The reaction of hexafluorocyclotriphosphazene, $N_3P_3F_6$ (1) with either m- or p-lithio-α-methyl styrene produces the corresponding (α-methyl ethenyl) phenyl pentafluorocyclotriphosphazenes in good yield. The compounds are clear,



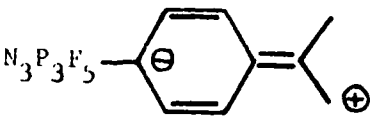
2. para isomer
3. meta isomer

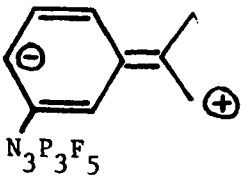
colorless liquids which are easily purified via distillation at reduced pressure. They were characterized by ^{1}H, ^{13}C, ^{19}F, ^{31}P NMR spectroscopy as well as infrared spectroscopy, mass spectrometry and elemental analysis.

The ^{1}H NMR spectra resemble those of the parent hydrocarbon with additional phosphorus proton coupling present in the aromatic region. In both 2 and 3, the proton chemical shifts appear downfield of α-methyl styrene, due to the strong electron accepting nature of the fluorophosphazene unit.[9,10] The ^{31}P and ^{19}F NMR spectra confirm the assignment of a monosubstituted phosphazene by exhibiting resonances due to two $\equiv PF_2$ centers and one $\equiv PFR$ center. The magnitude of the chemical shifts are consistent with previously reported aryl substituted fluorophosphazenes.[23] Finally, the ^{13}C NMR data support the assignment of the substitution pattern about the phenyl ring. The carbon spectra of 2 and 3 display four and six aryl carbon resonances, respectively, which is consistent with the para and meta derivatives.

Some features of the ^{13}C NMR spectra bear further discussion. Previous aryl carbon chemical shifts for fluorophosphazene derivatives were assigned by assuming that J_{PC} decreases with an increase in the number of intervening bonds between the atoms in question.[10] However by consideration of the spectrum of 3 and by use of selective decoupling techniques[24] it was found that $^{3}J_{PC} > {}^{2}J_{PC}$. The β-carbon chemical shift of the vinylidene carbon of styrene and α-methyl styrene derivatives have been used as a measure of the electronic perturbation induced by the substituent.[25] Using this criterion, the $N_3P_3F_5$ moiety ($\delta_{C\beta}$ = 115.9 ppm) is comparable to the strongly electron withdrawing nitro group ($\delta_{C\beta}$ = 115.8 for p - NO_2-$C_6H_4C(CH_3)=CH_2$[26]). This result is consistent with previous studies of the electron withdrawing effect of the fluorophosphazenes.[9,10] Another feature of the ^{13}C NMR data of interest is the difference in β-carbon chemical shift ($\Delta\delta$) between the meta (3) and para (2) isomers. The $\Delta\delta$ value (1.00 ppm) is midway between α-methyl styrenes with substituents which exhibit strong mesomeric interactions (e.g. NO_2) and those with substituents with no significant interaction (e.g. CF_3). This observation could be interpreted as showing a small to moderate conjugative

ability of the phosphazene unit. A similar suggestion was made by Harris et al. to rationalize NMR data of various arylphosphazenes.[11] Since a UV-photoelectron spectroscopy study of aryl fluorophosphazenes indicates little or no phosphazene aryl mesomeric interaction[10], we prefer an alternative and simpler model to rationalize the ^{13}C data. If one considers the two canonical structures representing removal of electron density from the olefin (and hence the β-carbon atom) by the phenyl group, it is clear that electrostatic stabilization of the negative

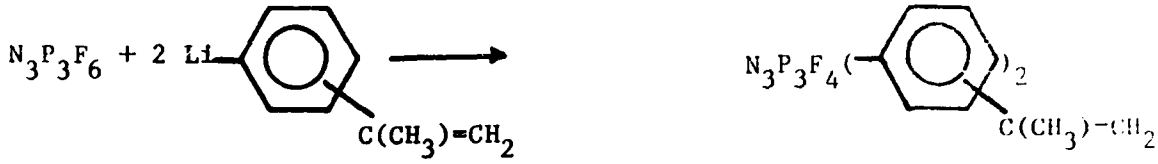




charge by the strongly electron withdrawing $N_3P_3F_5$ moiety is favored for the para isomer (3). Thus the electronic effect of the phosphazene is transmitted through the σ system.

The mass spectra of these new organophosphazenes are complex and dominated by ions generated from the organic moieties. However, a few salient features can be extracted. The base peak in the spectra of 2 and 3 is the molecular ion. The predominant fragmentation mode involves cheavage of the exocyclic group leaving the phosphazene intact which may be contrasted with phenyl fluorophosphazenes where aryl migration to a nitrogen atom and formation linear phosphazene ions is observed.[27] The relative intensities are similar in both isomers except that the intensity for loss of C_3H_5 is five times greater in 3 than in 2. This may be ascribed to the steric repulsion between the propenyl moiety and the phosphazene ring. Substitution in the meta position brings the propenyl residue into closer contact with both the geminal fluorine atom and the two transannular fluorine atoms, thus leading to a steric destabilization of 3.

If two equivalents of lithio-α-methyl styrene are allowed to react with 1. reasonable yields of the bis derivatives may isolated.



4 para isomer a. geminal, b.cis c.trans
5 meta isomer a. geminal, b.cis c.trans

While all three possible isomers of **4** and **5** were present in the crude reaction mixtures only the bis-cis (para-α-methyl styryl)-phosphazene, **4b** could be isolated in the pure state. The presence of the other isomers was confirmed by g.c., g.c.-mass spectrometry and NMR spectroscopy. The ^{1}H and ^{13}C spectra of the mixtures were not particularly helpful in this regard as they consist of numerous overlapping multiplets. However the ^{31}P NMR spectra are definitive. The trans isomer gives rise to a downfield second-order doublet and an upfield first order triplet from the $\equiv PFR$ and $\equiv PF_2$ centers respectively. In the case of the cis isomer, the spectrum contains the downfield doublet but the upfield triplet is now transformed into a doublet of doublets since the two fluorine atoms of the $\equiv PF_2$ center are no longer equivalent. The geminal isomer is readily identified by the pressure of a relatively small triplet arising from the $\equiv PR_2$ phosphorus atom interacting with the two equivalent $\equiv PFR$ centers. The ^{19}F NMR data corroborate the existence of all three isomers in the reaction mixture. The spectra of the cis, trans, and geminal isomers contain three, two and one unique fluorine resonance, respectively.

The ^{31}P and ^{19}F nmr spectra of the mixtures of isomers in both **4** and **5** show that the cis non-geminal isomers, **4b** and **5b**, are the major component in each case. A quantitative measure of the individual amounts of each isomer was obtained via gc and gc-mass spectrometry. Comparison of the gas chromatogram of **4b** with that of the mixture of isomers of **4** confirmed the cis isomer as the major constituent. The gc-mass spectrometry analysis of **5** shows the expected three components with

the largest gc peak assigned to (on the basis of the ^{31}P nmr spectrum) the cis isomer, **5b**. The first eluted compound shows a major fragmentation route involving cleavage of the aryl-phosphazene bond. This behavior is typical of a geminal isomer[27] and so allows assignment of **5a**. Geminal phosphazene isomers generally have the smallest gc retention times. The non-geminal isomers **5b** and **5c** show the expected fragmentation patterns[27] with formation of linear phosphazenes ions being an important feature. The intensities of the peaks assigned to the cis isomer are greater than those of the trans isomer. This is in agreement with the behavior of phenyl fluorocyclotriphosphazenes[27] thus adding addition evidence to the gc peak assignments. The isomer ratio (from gc) for **5a : 5b : 5c** is 1:2.8:1.1. The gc-mass spectrometry analysis of **4** shows the gem (**4a**) : cis (**4b**) : trans (**4c**) ratio to be 1:6.1:1.5. A curious feature of mass spectrum of the geminal, **4a**, isomer is the importance of the loss of a propenyl group and the formation of linear ions becoming competitive with phosphazene-aryl cleavage. The reason for the selective cleavage of the propenyl group in this case is unclear, but once it is severed from the aryl ring, there will be a more pronounced positive charge on that ring and it will be more likely to migrate to the adjacent ring nitrogen atom and eliminate as an aryl nitrene, a process which ultimately produces the linear phosphazene fragment seen in the mass spectrum.[27]

The observed substitution pattern for reactions of lithio-α-methyl styrenes with **1** are similar to that of the corresponding phenyl lithium reaction,[23] i.e. regio and stereoisomers are observed with non-geminal regioselectivity and cis stereoselectivity being observed. We have previously shown[6] that steric effects are reasonable for the formation of non-geminal, as opposed to the expected[2,7] geminal, products in the reactions of organolithium reagents with **1**. Further evidence for the importance of steric effects is found in the cis: trans ratio for the para vs meta (**5a,b**) α-methyl styrene derivatives. The cis selectivity is significantly reduced with the propenyl substituent in the meta

position where it might be expected to experience significant trans annular repulsions with another substituent in a cis configuration. The question of the cis preference in these reactions is an interesting one. If only steric effects were involved, then one would expect a strong trans preference, as is shown in the reactions of t-butyl lithium with 1[6]. We believe the observed the cis preference is due to an electrostatic interaction of the electron defecient aryl substituent on the phosphazene ring[9,10] and the electron rich incoming organolithium reagent. This interaction favors approach of the incoming reagent on the same side of the ring as the aryl substituent which is in place thus leading to the formation of the cis isomer. The fact that an approximately 1:1 cis: trans ratio is observed in the formation of p-(dimethylamino)phenyl tetrafluorocyclotriphosphazenes[28] is related to the exceptionally strong electron donating ability of the dimethylamino group. The transfer of electron density from the dimethylamino group to the phenyl ring reduces the electron deficient nature of the aryl groups and hence less electrostatic attraction with the incoming reagent occurs.

Acknowledgements. We wish to thank the Firestone Tire and Rubber Co. for a gift of $N_3P_3Cl_6$. The work was supported in part by the Office of Naval Research.

Supplementary Material Available: Table I showing major mass spectral fragments and their relative intensities. Ordering information is given on any current masthead page.

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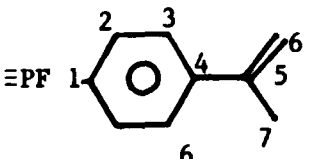
(18) All nmr (^{1}H, ^{13}C, ^{19}F, ^{31}P) chemical shifts are in ppm and coupling constants are in Hz. The positional designations, o, m and p, are with respect to the phosphazene. Ha and Hb refer to the olefinic protons trans and cis to the phenyl ring respectively.

(19) Numbers refer to:



(20) In cm^{-1}.

(21) Numbers refer to:

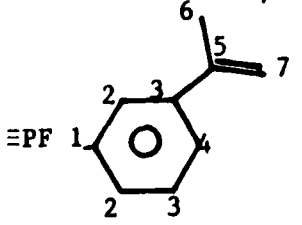


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Table I

Mass Spectrometry Data for (α-Methyl ethenyl)phenyl fluorocyclotriphosphazenes.

m/e	% Base		Ion
	2	3	
348	9	24	$N_3P_3F_5C_9H_{10}^+$
347	100	100	$N_3P_3F_5C_9H_9^+$
346	--	26	$N_3P_3F_5C_9H_8^+$
332	12	11	$N_3P_3F_5C_8H_6^+$
308	2	5	$N_3P_3F_5C_6H_6^+$
307	5	15	$N_3P_3F_5C_6H_5^+$
306	2	10	$N_3P_3F_5C_6H_4^+$
230	31	20	$N_3P_3F_5^+$
216	17	17	$N_2P_3F_5^+$
197	11	12	$N_2P_3F_4^+$
173.5	4	3	$N_3P_3F_5C_9H_9^{2+}$
171	9	7	$NP_2F_5^+$
152	7	8	$NP_2F_4^+$
117	60	47	$C_9H_9^+$
116	39	39	$C_9H_8^+$ or $N_2PF_3^+$
115	68	89	$C_9H_7^+$
114	12	9	$NP_2F_2^+$
102	9	10	NPF_3^+ or $C_8H_6^+$
91	16	18	$C_6H_5N^+$ or $C_7H_7^+$
89	11	16	$C_7H_5^+$
77	7	7	$C_6H_5^+$
76	6	8	$C_6H_4^+$ or N_2P^+
75	10	11	$C_6H_3^+$
69	13	10	PF_2^+ or P_2N^+
65	6	7	$C_5H_5^+$
63	13	15	$C_5H_3^+$
51	13	11	HPF^+ or $C_4H_3^+$
31	10	11	PF^+

m/e	% Base			Ion
	4b	4c	4a	
446	15	9	-	$N_3P_3F_4C_{18}H_{19}^+$
445	87	100	100	$N_3P_3F_4C_{18}H_{18}^+$
444	30	36	-	$N_3P_3F_4C_{18}H_{17}^+$
430	7	-	-	$N_3P_3F_4C_{17}H_{15}^+$
429	18	13	4	$N_3P_3F_4C_{17}H_{14}^+$
405	-	-	73	$N_3P_3F_4C_{15}H_{14}^+$
404	-	-	97	$N_3P_3F_4C_{15}H_{13}^+$
364	14	-	9	$N_3P_3F_4C_{12}H_9^+$
328	7	-	17	$N_3P_3F_4C_9H_9^+$
222.5	7	-	-	$N_3P_3F_4C_{18}H_{18}^{2+}$
211	7	-	5	$N_3P_3F_4^+$
197	60	15	19	$N_2P_3F_4^+$
178	5	-	3	$N_2P_3F_3^+$
152	16	-	4	$NP_2F_4^+$
117	23	13	-	$C_9H_9^+$
116	34	10	6	$C_9H_8^+$ or $N_2PF_3^+$
115	100	46	30	$C_9H_7^+$
102	15	3	-	NPF_3^+ or $C_8H_6^+$
91	37	10	13	$NC_6H_5^+$ or $C_7H_7^+$
89	13	2	3	$C_7H_5^+$ or $NC_6H_3^+$
77	13	2	41	$C_6H_5^+$
76	6	-	3	N_2P^+ or $C_6H_4^+$
65	9	2	2	$C_5H_5^+$
63	9	2	2	$C_5H_3^+$
51	10	2	24	$C_4H_3^+$ or HPF^+

m/e	% Base			Ion
	5b	5c	5a	
446	15	---	12	$N_3P_3F_4C_{18}H_{19}^+$
445	100	100	80	$N_3P_3F_4C_{18}H_{18}^+$
444	95	---	92	$N_3P_3F_4C_{18}H_{17}^+$
430	9	2	7	$N_3P_3F_4C_{17}H_{15}^+$
404	6	4	10	$N_3P_3F_4C_{15}H_{13}^+$
328	7	3	32	$N_3P_3F_4C_9H_9^+$
222.5	3	1	1	$N_3P_3F_4C_{18}H_{18}^{++}$
197	27	10	8	$N_2P_3F_4^+$
152	---	---	6	$NP_2F_4^+$
117	12	6	9	$C_9H_9^+$
116	17	8	22	$C_9H_8^+$ or $N_2PF_3^+$
115	78	30	100	$C_9H_7^+$ or $NC_8H_5^+$
103	4	1	4	$C_8H_7^+$
102	7	4	18	$C_8H_6^+$ or NPF_3^+
101	8	1	7	$C_8H_5^+$
91	25	8	58	$C_6H_5N^+$ or $C_7H_7^+$
89	8	3	12	$C_7H_5^+$ or $C_6H_3N^+$
77	11	3	13	$C_6H_5^+$
76	---	---	11	N_2P^+ or $C_6H_4^+$
65	5	2	13	$C_5H_5^+$
63	6	2	8	$C_5H_3^+$
51	7	2	12	$C_4H_3^+$ or HPF^+

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